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## Research Paper

## 10,000 years of climate control over carbon accumulation in an Iberian bog (southwestern Europe)



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## ABSTRACT

The northwest region of the Iberian Peninsula is home to a unique ecosystem of bogs, which are particularly sensitive to projected climate change. In this context, the rate of carbon (C) accumulation in Chao de Veiga Mol, an intact raised bog, was analysed. Changes in the accumulation rate over the past 10 millennia were determined in a peat core of 847 cm in depth, with a high mean rate of peat growth ( $11 \text{ yr cm}^{-1}$ ,  $0.09 \text{ cm yr}^{-1}$ ). An age-depth model was generated from 22  $^{14}\text{C}$  dates and fallout radio-nuclides. Chronological, stratigraphical and physico-chemical data confirmed the existence of a single cycle of peat formation throughout the Holocene and the formation of ombrotrophic peat 9500 years ago. The total mean C content was 50.2%, and over 10 millennia  $583 \text{ kg C m}^{-2}$  accumulated at a mean rate of  $35.3 \text{ g C m}^{-2} \text{ yr}^{-1}$ , with a long-term (apparent) rate of carbon accumulation in the catotelm of  $59.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ . These values are much higher than reported for other Iberian peatlands and are amongst the highest documented for peatlands in the northern hemisphere. The dynamics of C accumulation and other measured parameters reveals important variations throughout the Holocene. They could be associated with the main climatic events described in the northern hemisphere and are highly consistent with models established for northern latitudes. The Chao de Veiga Mol raised bog is unique and of great potential value for carrying out high resolution palaeoenvironmental studies, especially in relation to regional and local modulations in southern Europe.

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## 1. Introduction

In the context of the current global climate change scenario, knowledge about carbon cycling and sequestration in European soil systems has advanced in recent years (de Brogniez et al., 2015), and local patterns of palaeoenvironmental evolution have become

increasingly important for improving general predictive climate models (Limpens et al., 2008). In this sense, peatlands play a fundamental role in the global carbon cycle and may become either enhanced carbon sinks or sources under future climate change (Charman et al., 2015). Accumulation of peat occurs as a result of a series of complex hydrological, climatic, chemical, physical and biological interactions that favour a positive balance between production of necromass and mineralization of soil organic matter (Mäkilä and Saarnisto, 2008). Increased productivity and/or decreased decomposition imply an increase in the rates of peat accumulation (Francez and Vasander, 1995; Kuhry and Vitt, 1996). These three factors that act on the formation of peat and the accumulation of carbon will be conditioned by the balances

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established between the climatic conditions, the composition of the plant remains and the soil environment (Moore, 1975; Korhola et al., 2010; Laine et al., 2015).

Loss of mass occurs continuously during peatland formation; however, the kinetics of degradation varies greatly within the diplothemlic structure. Peatlands are organized in a double-layer or diplothemlic hydrological-structural system (Ingram, 1978). In acrotelm, a top layer with high conductivity and fluctuating hydromorphism, partially aerobic conditions allow for relatively significant microbial activity. Underneath, the catotelmic layer develops, permanently hydromorphic and anoxic, with very low microbial activity (Clymo, 1984). The formation and evolution of peat is highly conditioned by the behaviour of these two layers, which depends to a large extent on the climatic conditions of each moment. Under the permanently anoxic conditions of the catotelm, degradation occurs extremely slowly, although it does not stop. By contrast, substantial loss of necromass occurs in the aerobic layer of the acrotelm, with between 10% and 20% becoming incorporated in the catotelm (Clymo, 1984). The dynamics of the equilibrium between accumulation of peat in the catotelm and loss of mass in the acrotelm are linked to fluctuations in the environmental and edaphic conditions (Martínez-Cortizas et al., 2007; Philben et al., 2014).

The peatlands response to environmental variations enables climate reconstruction by analysis of the variations in carbon accumulation rates (Loisel and Yu, 2013; Charman et al., 2015; Lamentowicz et al., 2016). An increase in accumulation rates may reflect climate conditions that favour productivity, edaphic moisture and/or a positive balance between precipitation and evaporation. Ombrotrophic peatlands (bogs) are particularly sensitive to the synchronization between climate dynamics and peat formation as the inputs in the hydrologic balance are exclusively atmospheric, and the relationship between precipitation and evapotranspiration becomes particularly important (Charman and Mäkilä, 2003).

The Iberian peatlands cover an area of ca. 20,000 ha (Heras et al., 2017), of which at least half are located in the NW Iberian

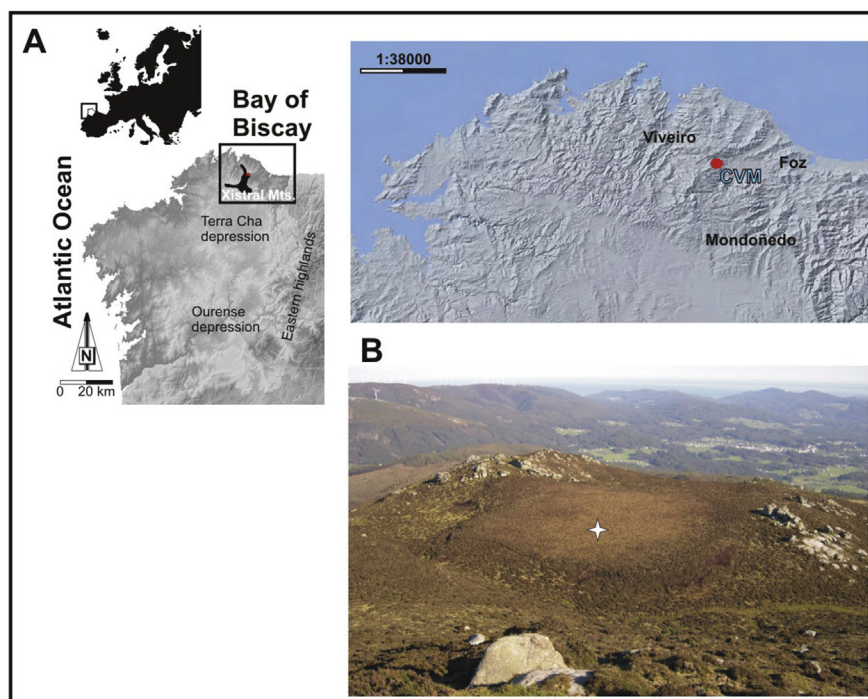
Peninsula, the main reservoir of terrestrial carbon (Pontevedra-Pombal et al., 2017) and an area particularly sensitive to climate change (Giorgia and Lionello, 2008).

Blanket bogs and raised bogs (ombrotrophic peatlands) occur at the southern limit of their distribution in the northern sector and especially in the NW Iberian Peninsula (Pontevedra-Pombal et al., 2006). These bogs were formed during the Holocene and they are essential elements for understanding the environmental changes that have taken place in southern Europe. An unusual raised bog has recently been identified in the NW Iberian Peninsula within this highly restricted peatland type. Due to its characteristic of sensitivity, temporal resolution, chronology and typology, with growth rates at least two times higher than in other peatlands in southern Europe it can be considered to be unique within this territory. Studies of carbon accumulation rates in the Iberian peatlands are extremely scarce and incomplete (Pontevedra-Pombal et al., 2006), and to date it has not been possible to perform high resolution analysis for the Holocene.

The purpose of the present study was to carry out high resolution chronological analysis of this unique mire to explore changes in carbon accumulation rates during the Holocene and to compare the information obtained with existing local, regional and global palaeoclimatic data in order to detect connections or anomalies relative to the general palaeoclimatic pattern in southern Europe.

## 2. Study area

The study area ( $43^{\circ}20'N$ – $43^{\circ}40'N$ ;  $7^{\circ}20'W$ – $7^{\circ}43'W$ ) is located in the highest elevations of the *Serras Septentrionais* of Galicia in the NW Iberian Peninsula (Fig. 1). The nucleus of these mountains is formed by the O Xistral Mountain Range, which is slightly higher than 1000 m a.s.l., the mountains of O Cadramón, the A Toxiza granodioritic batholith and a cohort of small mountains. The maximum elevation reached is 1060 m a.s.l., and most of the land lies between 700 and 900 m a.s.l. The lithology in the western zone consists of metamorphic materials, amongst which the Xistral



**Figure 1.** (A) Location of the study area. (B) General view of the CVM raised bog, with a white star marking the position of core sampling.

orthoquartzites dominate in terms of extension, whereas granitic rocks dominate in the eastern zones (Parga-Pondal and Aleixandre, 1966).

This mountainous belt is the best example of a very wet and cool environment in southern Europe, with a sharp ombrothermic gradient from the coast to the mountainous areas. At the summit, rainfall is between 1400 and 1800 mm, the effective fog-precipitation exceeds 5000 mm (Pontevedra-Pombal et al., 2014) and the mean temperature ranges from 7 to 10 °C. The rainfall gradient is close to 100 mm per 100 m of elevation, and the thermometric gradient is  $-0.67$  °C per 100 m altitude. The seasonal variation in precipitation is the lowest recorded in the Iberian Peninsula.

The morphology is characterized by staggered flat surfaces, resulting from the dislocation of a major surface and differential tilting during various stages of the Tertiary. These surfaces are strongly incised by valleys that discharge directly into the Bay of Biscay. The upper parts of some rivers, affected during the Pleistocene by low altitude glaciation (<1000 m a.s.l.) and by a strong oceanic influence, are surrounded by more gently sloping valleys.

### 3. Material and methods

#### 3.1. Chao de Veiga Mol mire

The Chao de Veiga Mol (CVM) mire ( $43^{\circ}32'34''\text{N}$ ,  $7^{\circ}30'13''\text{W}$ ) is a raised bog located in the extreme northeast of the Xistral Mountain Range, at an elevation of 700 m a.s.l. and 15 km south of the coast of the Bay of Biscay (Fig. 1). It occupies a palaeo-glacial cirque excavated in a two-mica granite (Valcárcel et al., 2015), with peat of thickness 9 m thick dating back to 10 cal. ka BP (ages are expressed as calibrated years before present; cal. yr BP or cal. ka BP).

The mean annual temperature in the area is  $7.0$  °C, and the mean annual rainwater precipitation is 1700 mm.

The mire ecosystem (Fig. 1) occupies a sub-basin of area 45 ha, consisting of a main ombrotrophic dome of area 2.10 ha (confined raised bog), two side domes of 0.5 and 0.9 ha (non-confined raised bogs), three minerogenic fens of 1.1, 1.0 and 1.7 ha (marginal fens) and heaths on peaty soils. The study area belongs to the Atlantic biogeographic region.

The microtopography and water table level determine the current different microhabitats that shelter dry and wet heaths dominated by *Erica mackaiana* Bab; laws of *Carex durieui* Steudel ex Kunze, *Eriophorum angustifolium* Honck., *Molinia caerulea* (L.) Moench, *Sphagnum* spp., and *Drosera rotundifolia* L., intermixed with scattered specimens of *E. mackaiana*, besides waterlogged lawns with *Sphagnum cuspidatum* Hoffm, *Agrostis stolonifera* L. and *Juncus bulbosus* L. as the most common species.

#### 3.2. Peat coring

To determine the depth of the peat, measurements were made along ten transects, each separated by a distance of 5 m, on the longest axis of the bog. In each transect, the thickness of the peat was measured every 3 m. The maximum depth was 915 cm. In the area where the peat was thickest, two peat profiles were extracted, to a maximum depth of 847 cm.

The cores were extracted with a Wardenaar corer (10 cm  $\times$  10 cm  $\times$  100 cm) for the upper 100 cm and a Russian peat sampler (GYK type, length 50 cm, diameter 5 cm) for the rest. A 10 cm overlap between the sub-cores and their stratigraphic control was established. Fresh cores were sliced with a stainless-steel knife and the core slices were then wrapped in plastic bags and covered with aluminium foil. The saw blade was washed with bi-distilled water after cutting each sample. Samples were taken

every centimetre in the top 100 cm, and at 2 cm slices in the rest of core. Two samples were also taken at the surface of the peat-vegetation interface. These samples were each separated into four sub-samples. One was frozen at  $-10$  °C, the second was maintained at  $4$  °C, the third was lyophilized and the fourth was dried at  $105$  °C. The latter two sub-samples were milled finely in an agate mortar, homogenized and stored in the dark, without humidity and at less than  $6$  °C.

### 3.3. Chronology

#### 3.3.1. Radiocarbon data

Twenty-two bulk peat samples were sent to the Ångström Laboratory (Uppsala University, Sweden) and the Center for Applied Isotope Studies (University of Georgia, USA) for radiocarbon AMS dating, to establish patterns of bog development. The selected samples, devoid of woody debris and with any rootlets removed, present the appropriate conditions for radiocarbon analysis (Holmquist et al., 2016). The  $^{14}\text{C}$  dates (Table 1) were calibrated using CALIB 7.1 (Stuiver et al., 2015; <http://calib.qub.ac.uk/calib>) with the IntCal13 curve (Reimer et al., 2013).

#### 3.3.2. Radionuclide data

The top thirty samples taken from the CVM core were used to determine the concentrations of fallout  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$ ,  $^{214}\text{Pb}$  and  $^{241}\text{Am}$  (Table 2, Fig. 2), in order to establish geochronological patterns of recent peat accumulation using gamma spectrometry and data processed using the constant rate of supply (CRS) model (Appleby and Oldfield, 1978; Appleby, 2001). These determinations were carried out at the Consolidated Radioisotope Facility (CoRiF) at the University of Plymouth, following the methodology described by Appleby (2001).

The instrument was calibrated using peat material spiked with a certified, traceable mixed radioactive standard (QCYA178402012) supplied by Eckert & Ziegler Analytics (Georgia, USA). All calibration relationships were derived using EG&G GammaVision software and verified by inter-laboratory comparison tests with materials

**Table 1**  
AMS-radiocarbon data with  $2\sigma$  range of calibration from CVM raised bog.

Sample	Material	Depth (cm)	Age $^{14}\text{C}$ (BP)	Error $^{14}\text{C}$ age (BP)	Age ranges (cal. yr BP)	Lab. Code
CUR-13	peat	14.5	modern			UGAMS-8991
CUR-25	peat	26.5	60	20	33–253	UGAMS-8992
CUR-50	peat	51.5	270	20	285–426	UGAMS-8993
CUR-100	peat	101.5	790	25	675–738	UGAMS-8994
CUR-125	peat	151	1220	25	1064–1241	UGAMS-8995
CUR-150	peat	201	1640	25	1418–1610	UGAMS-8996
CUR-175	peat	251	2100	25	1999–2137	UGAMS-8997
CUR-200	peat	301	2850	25	2878–3039	UGAMS-8998
CUR-262	peat	425	3890	25	4248–4413	UGAMS-25538
CUR-306	peat	513	4520	35	5048–5307	UGAMS-25539
CUR-313	peat	527	4870	25	5587–5647	UGAMS-9236
CUR-325	peat	551	5200	25	5916–5991	UGAMS-9002
CUR-350	peat	601	5640	30	6321–6490	UGAMS-9003
CUR-368	peat	637	6160	30	6972–7162	UGAMS-9004
CUR-375	peat	651	6320	30	7172–7308	UGAMS-9005
CUR-391	peat	683	6980	30	7721–7927	UGAMS-9006
CUR-400	peat	701	7010	30	7786–7935	UGAMS-9007
CUR-424	peat	749	7740	30	8444–8589	UGAMS-9008
CUR-452	peat	805	8040	30	8778–9021	UGAMS-9009
CUR-466	peat	833	8550	30	9493–9547	UGAMS-9010
CUR-473	peat	846.25	8640	55	9522–9742	Ua-34556
CUR-250 <sup>a</sup>	peat	401	2980	25	3070–3206	UGAMS-8999
CUR-276 <sup>a</sup>	peat	453	3540	25	3722–3896	UGAMS-9000
CUR-301 <sup>a</sup>	peat	503	3680	25	3926–4090	UGAMS-9001

<sup>a</sup> Contaminated samples.



**Table 2**

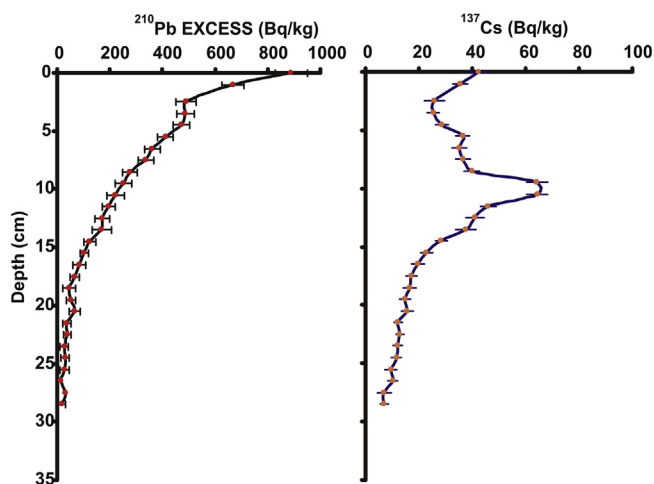
Activity concentrations of the key fallout radionuclides  $^{137}\text{Cs}$  and excess  $^{210}\text{Pb}$  against peat core mass depth (where uncertainty is expressed as  $2\sigma$  based on counting statistics and n.d. indicates activity below limit of detection).

Sample depth (cm)	Mass depth ( $\text{g cm}^{-2}$ )	$^{137}\text{Cs}$ ( $\text{Bq kg}^{-1}$ )	$^{210}\text{Pb}_{\text{xs}}$ ( $\text{Bq kg}^{-1}$ )
0	0.19	$42.49 \pm 4.09$	$888.87 \pm 61.00$
1	0.35	$35.61 \pm 2.77$	$669.25 \pm 41.82$
2.5	0.53	$25.92 \pm 3.79$	$489.33 \pm 38.82$
3.5	0.69	$25.40 \pm 2.32$	$486.89 \pm 33.87$
4.5	0.84	$28.58 \pm 2.34$	$472.98 \pm 30.86$
5.5	1.01	$36.45 \pm 2.68$	$411.24 \pm 29.81$
6.5	1.17	$35.24 \pm 2.75$	$360.61 \pm 29.83$
7.5	1.34	$36.57 \pm 2.91$	$337.02 \pm 29.73$
8.5	1.50	$39.83 \pm 3.05$	$276.72 \pm 27.00$
9.5	1.66	$64.24 \pm 4.05$	$252.09 \pm 30.73$
10.5	1.82	$64.36 \pm 3.94$	$221.65 \pm 32.81$
11.5	1.98	$46.02 \pm 3.06$	$195.65 \pm 23.83$
12.5	2.14	$40.91 \pm 3.44$	$171.57 \pm 27.69$
13.5	2.30	$37.55 \pm 3.82$	$169.20 \pm 36.62$
14.5	2.47	$28.40 \pm 2.35$	$124.12 \pm 24.09$
15.5	2.63	$22.93 \pm 2.14$	$102.50 \pm 15.92$
16.5	2.80	$19.72 \pm 2.47$	$84.17 \pm 24.29$
17.5	2.95	$17.28 \pm 2.04$	$66.37 \pm 18.18$
18.5	3.11	$16.67 \pm 2.37$	$45.32 \pm 23.90$
19.5	3.26	$14.89 \pm 2.01$	$53.16 \pm 16.68$
20.5	3.42	$15.62 \pm 2.20$	$66.26 \pm 21.50$
21.5	3.59	$12.24 \pm 1.68$	$36.07 \pm 15.10$
22.5	3.77	$12.86 \pm 1.63$	$39.50 \pm 13.05$
23.5	3.95	$12.00 \pm 1.66$	$27.40 \pm 15.85$
24.5	4.11	$11.70 \pm 1.91$	$29.91 \pm 16.31$
25.5	4.27	$9.49 \pm 2.26$	$26.83 \pm 17.66$
26.5	4.45	$10.18 \pm 1.90$	n.d.
27.5	4.66	$6.97 \pm 2.53$	n.d.
28.5	4.86	$6.96 \pm 1.61$	$16.76 \pm 14.93$
29.5	5.06	n.d.	n.d.
30.5	5.28	n.d.	n.d.

supplied by the IAEA (namely the world-wide proficiency test with moss soil: IAEA-CU-2009-03).

Total  $^{210}\text{Pb}$  was measured and its unsupported component was calculated by subtracting the  $^{226}\text{Ra}$  activity, which in turn was measured by the gamma emissions of  $^{214}\text{Pb}$ .

To produce activity profiles against depth (Fig. 2) from the core sample for geochronological purposes, core samples were counted for at least 90,000 s to the depth limit of fallout  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  (Table 2), i.e. until the activity concentrations of these radionuclides fell below the Minimum Detectable Activity (MDA). All activity concentration data were decay-corrected to the date of sampling.



**Figure 2.** Fallout  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  activity profiles from the CVM raised bog.

We used the Bacon age-modelling software (Blaauw and Christen, 2011) to construct an age-depth model based on all  $^{210}\text{Pb}$  and  $^{14}\text{C}$  dates (Fig. 3). This model simulates the temporal deposition by assuming piece-wise linear accumulation, with accumulation rates and the associated variability between neighbouring depths constrained by prior information. All settings were default, except for the section thickness, which was set at 10 cm (top-right panel of Fig. 3). The information we used to adapt the section thickness to 10 cm had to do with the length of the core (>800 cm). Section thickness was adapted to 10 cm, because with thinner and thus more sections (using the default 5 cm), too many parameters would have to be estimated, which could result in runaway MCMC iterations. The model was based on more than 5000 stored MCMC (Markov chain Monte Carlo) iterations and has a stable run (top-left panel of Fig. 3). The peat core analysed represents the last 10 millennia of the Holocene (Table 1; Fig. 3).

### 3.4. Physico-chemical analysis

Several key properties were analysed in order to define the geochemical characteristics of the genesis of CVM and its trophic evolution. Peat dry bulk density (BD) was determined following the method described by Lynn et al. (1974). Inorganic ash content was obtained by drying at 600 °C, and the results were expressed as the percentage of dry peat mass (105 °C). The pH in distilled water ( $\text{pH}_w$ ) was measured in wet peat samples using a specific peat volume:solution ratio for each sample, calculated to maintain a weight:solution ratio (1:2.5). The 'von Post scale' of humification was evaluated in all samples (von Post, 1937). With this index, the degree of evolution of the peat is characterized according to parameters such as the size and differentiation of the plant fibres or remains, the turbidity of the water extracted by squeezing or the amount of material that escapes between the fingers when pressed inside the hand, thus constructing a scale of 10 categories from lowest to highest degree of evolution (H1–H10). The categories H9–H10 correspond to sapric materials, H5–H1 to fibric materials, and the intermediate categories would be of a hemic nature. The concentrations of exchangeable Ca and Mg extracted in wet peat samples were determined by flame atomic absorption spectrophotometry (Peech et al., 1947), and the Ca/Mg molar ratios were calculated.

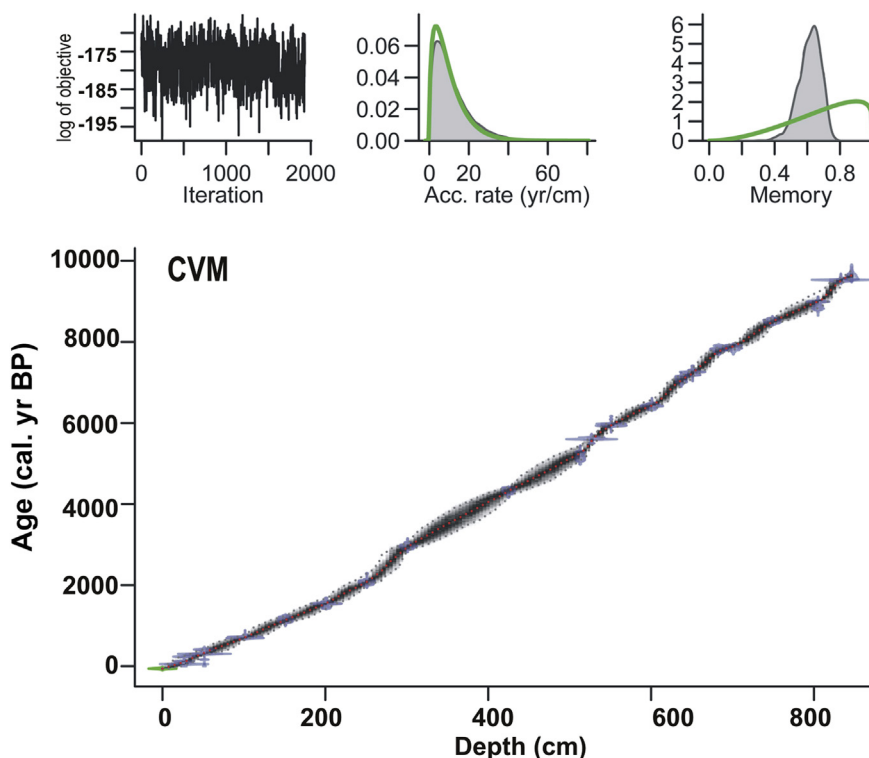
### 3.5. Total carbon content

Total carbon (C) in dried and milled samples was quantified with a Leco CHN 1000 autoanalyzer, by complete combustion at 1000 °C and infrared detection band of the  $\text{CO}_2$  released, with absolute error less than 0.3%. The equipment was calibrated and verified using different reference materials (EDTA-502-092, SOIL-502-309, SOIL-502-308, COAL-501-001, COAL-501-002). The presence of carbonates was unlikely, as indicated by the very high to high acidity (range of pH values 3.9–4.5), low inorganic ash content ( $2.6\% \pm 1.7\%$ ) and lithology, and the total C measured is comparable to the total organic C.

### 3.6. Peat and carbon accumulation rates

The typology and exceptional development of this peat bog, a high stratigraphic resolution in the subsamples, which varies between 1 and 2 cm across the entire cores, and a well-defined chronological model makes Chao de Veiga Mol a unique candidate for exploring the paleoecological signals in the Iberian Peninsula.

The vertical peat growth rates (PGR;  $\text{cm yr}^{-1}$ ) were calculated from the age-model and the thickness of the peat samples. The



**Figure 3.** Age-depth model based on  $^{14}\text{C}$  and  $^{210}\text{Pb}$  results and produced using BACON software. Top panels show the MCMC (Markov chain Monte Carlo) run (left), prior (empty curve) and posterior (grey-filled curve) distributions for accumulation rate (middle) and its variability (right). Main panel shows the calibrated  $^{14}\text{C}$  (blue) and  $^{210}\text{Pb}$  (green) dates, and the age-depth model where grey-scales indicate all possible age-depth models, and dotted lines indicate the mean and 95% confidence ranges.

carbon accumulation rates (CAR;  $\text{g C m}^{-2} \text{yr}^{-1}$ ) were calculated for each, based on the method proposed by Tolonen and Turunen (1996), as the relationship between the product of carbon content, bulk density (BD) and thickness of each sample and the time interval represented by each sample. We also calculated the long-term apparent rate of carbon accumulation (LORCA), that is, the average carbon accumulation rate (CAR) for the entire peat core (Tolonen et al., 1992; Vitt et al., 2000; Gorham et al., 2003). The LORCA was determined for the catotelm, 250–9700 years ago (40–847 cm); oxic and actively decomposing peat in the acrotelm was excluded (Turunen et al., 2004).

## 4. Results

### 4.1. Pedogenesis and trophic conditions of the peatland

In the stratigraphic profile of CVM (Fig. 4), the 15 cm basal peat shows a black colour and a degree of humification of H8–H9 on the von Post scale. In contrast, the rest of the profile shows a reddish brown peat, with a degree of humification H2–H3 on the von Post scale, and few visible differences down to a depth of 830 cm (except for accumulated wood remains at some levels, some darker H4–H5 levels and fluctuations in the proportion of *Sphagnum* remains).

The combined distribution within the peat profile of the bulk density (BD), inorganic ash content, and Ca/Mg molar ratio (Fig. 5), and the presence of a dome, indicate the ombrotrophic nature of the CVM bog and are consistent with those considered representative of ombrotrophic peats (Shotyk, 1996). The temporal changes in these properties indicate a strong, rapid transition to ombrotrophization that began ca. 9500 cal. yr BP and was definitely established at a depth of 820 cm (ca. 9300 cal. yr BP).

The C/Ash ratio clearly discriminates three groups of samples (Fig. 6) associated respectively with the minerogenic phase, the ombrotrophic phase and the surface of the bog. The observed effect on the minerotrophic peat is likely related to an interaction between the peat and the underlying mineral substrate, whereas the surface samples contain mineral salts produced by the incomplete degradation and recycling of plant biomass and, probably, sea-salt spray.

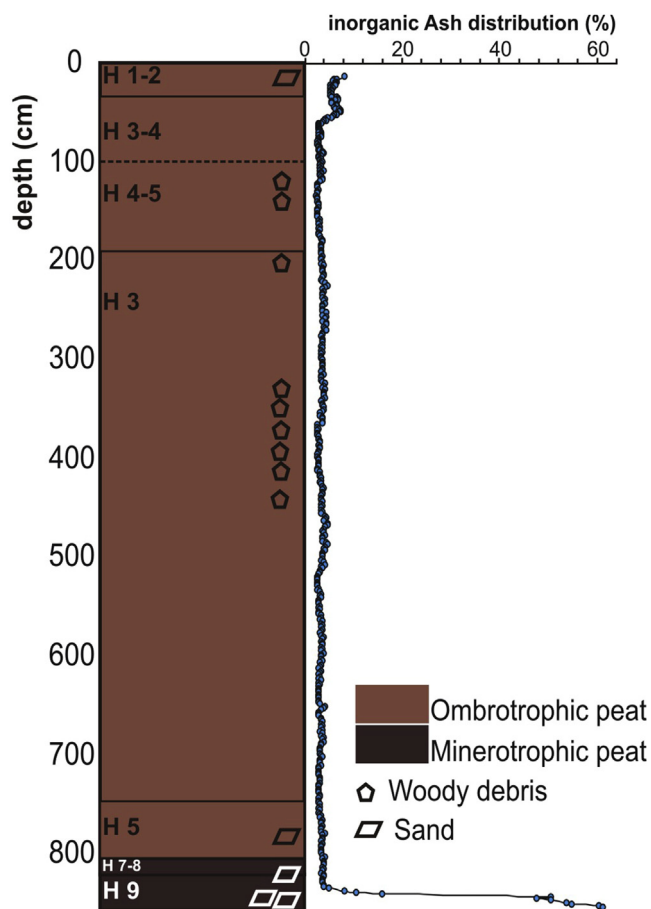
### 4.2. Content and distribution of total organic carbon

The total mean organic C content in the CVM profile is  $50.2\% \pm 3.7\%$ , although maximum values of 55% are reached in the ombrotrophic phase, and a minimum of 23% in the minerotrophic phase.

The clear increase in the C content observed towards the bottom of the profile (Fig. 5) is associated with the processes of decomposition and loss of mass, with values of 44.5% in the surface samples and of 55% C in the deeper ombrotrophic layers (824 cm). The C enrichment is much more intense in the upper 50 cm, varying from 44.5% to 49%, possibly reflecting the transition between the acrotelm and catotelm.

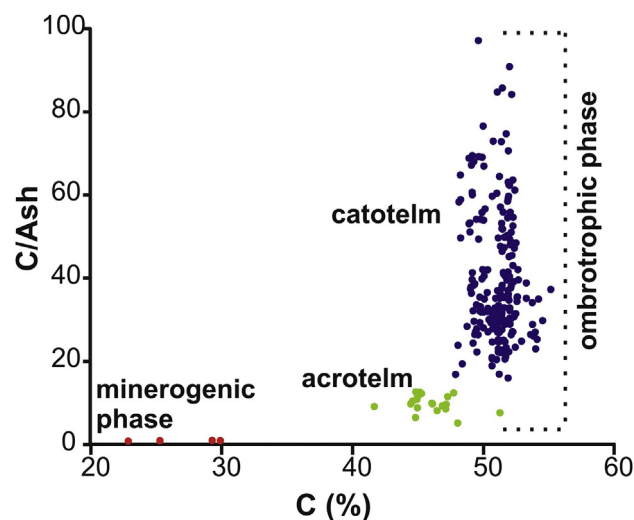
### 4.3. Peat and carbon accumulation rates

The long-term mean vertical peat growth rate (PGR) in the CVM raised bog was  $0.9 \text{ mm yr}^{-1}$  ( $11 \text{ yr cm}^{-1}$ ). Total carbon accumulation was  $583 \text{ kg C m}^{-2}$  over 10,000 years, the LORCA was  $59.9 \text{ g C m}^{-2} \text{yr}^{-1}$  and the average CAR was  $35.3 \pm 12 \text{ g C m}^{-2} \text{yr}^{-1}$ . The average deviation from the CAR calculated for each sample does not exceed 3%, with a variation between 7% and 1%.



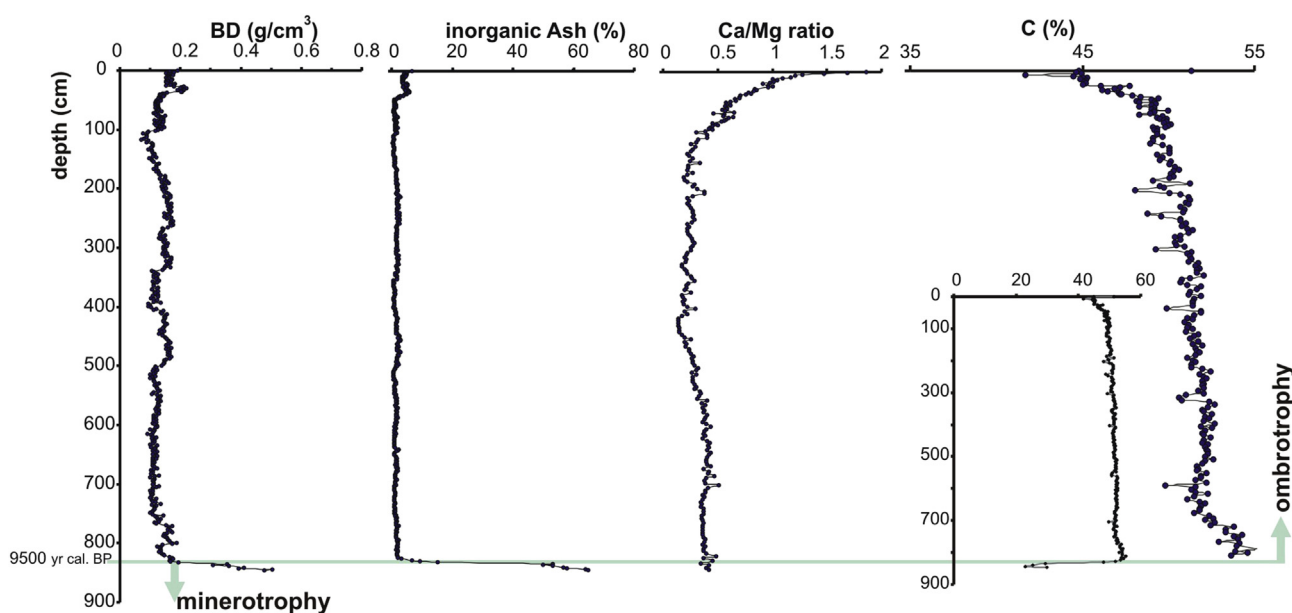
**Figure 4.** Morphostratigraphy of the CVM raised bog. Hx indicates the range of evolution of the peat on the von Post scale.

Calculation of C accumulation for different periods of the Holocene revealed various apparent differentiated phases. At the



**Figure 6.** Relationship between organic carbon and inorganic matter (inorganic ash) throughout genesis and evolution of the CVM bog.

start of the peat formation and during transformation from a minerotrophic to an ombrotrophic system (ca. 10–8 cal. ka BP), the LORCA ( $65 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) was higher than the mean value for the Holocene. In the following 3 millennia (ca. 8–5 cal. ka BP), the LORCA was lower than the mean value ( $10.5\text{--}30 \text{ g C m}^{-2} \text{ yr}^{-1}$ ), although an increase was observed between ca. 7 and 6 cal. ka BP. Between ca. 5 and 3 cal. ka BP, the LORCA was higher than  $52 \text{ g C m}^{-2} \text{ yr}^{-1}$ , and a decrease was then observed between ca. 3 and 2 cal. ka BP ( $24 \text{ g C m}^{-2} \text{ yr}^{-1}$ ). A new increase in carbon accumulation, the largest throughout the entire Holocene, was detected between ca. 2 and 1 cal. ka BP ( $58 \text{ g C m}^{-2} \text{ yr}^{-1}$ ). The LORCA value for the period between the beginnings of the last millennium until 250 years ago is very close to the mean value for the Holocene.



**Figure 5.** Ombrotrophic properties of the CVM bog: bulk density (BD), inorganic ash content (Ash), Ca/Mg ratio and carbon (C). In the larger graph of carbon, the minerogenic section was removed to facilitate observation of fluctuations in the ombrotrophic phase.

## 5. Discussion

### 5.1. Chronology and Pedogenesis

The age-depth model, the stratigraphic descriptions and the physico-chemical properties determined in the Chao de Veiga Mol (CVM) core confirm the existence of a single peat forming cycle throughout the Holocene, without any apparent hiatuses. The basal soil material was not recovered, although it must have been formed after the Last Glacial Maximum, 18–15 cal. ka BP (Pérez-Alberti and Valcárcel, 1997), during which time a cirque was colmatation and occupied by the peatland. The ombrotrophization phase was consolidated by ca. 9.5 cal. ka BP. The rapid evolution of shallow glacial structures from the Würm stage to raised bogs and the brief minerotrophic phase that led to oligotrophic and finally ombrotrophic conditions is similar to that described for British raised bogs ca. 9.9 cal. ka BP (Hughes et al., 2000; Hughes and Barber, 2004).

In CVM, the mean bulk density value ( $0.1291 \text{ g cm}^{-3}$ ), a very important parameter for the final calculation of carbon accumulation rates shows small variations that indicate the absence of erosion or compaction processes. These values are similar to those determined in other ombrotrophic peatlands in the northwest of the Iberian Peninsula (Pontevedra-Pombal, 2002; Pontevedra-Pombal et al., 2006) but also in ombrotrophic peatlands in the northern hemisphere (Shotyk, 1996; Jensen, 1997; Cloy et al., 2009).

The carbon content of the CVM is similar to that for other ombrotrophic peats in the NW Iberian Peninsula (Pontevedra-Pombal et al., 2006) and consistent with the mean values established for bogs with a degree of humification between H1 and H5 on the von Post scale (Naucke et al., 1993). It is higher than the mean carbon content in the northernmost peatlands ( $>45^\circ\text{N}$ ) from the northern hemisphere and similar to the values established for western European islands peatlands (Loisel et al., 2014).

The depth-related increase in the C content in the CVM follows the same pattern observed in other ombrotrophic peatlands in the Iberian Peninsula (Pontevedra-Pombal, 2002; Martínez-Cortizas et al., 2016; Pérez-Obiol et al., 2016) and in northern European ones (Updegraff et al., 1995; Malmer and Wallén, 2004).

The mass loss due to the decay of organic matter causes a relative enrichment of carbon, coupled to the selective preservation and/or diagenesis of C-enriched components (Pontevedra-Pombal et al., 2004; Kaal et al., 2007). With decay of organic matter, gradual enrichment with aliphatic carbon takes place in these peatlands, with greater amounts of highly aromatic compounds in the upper few centimetres and an age-related decrease in the polysaccharide content. This has been observed as a general trend in peatlands at different latitudes (Hammond et al., 1985; Fox et al., 1994; Wachendorf et al., 1996; Lu et al., 2000). The increase in C is due to the accumulation of recalcitrant forms of the original peat and neoformations produced by microbial activity (Brown et al., 1989; Schnitzer et al., 1990; Amelung et al., 1997; Disnar et al., 2008; Schellekens et al., 2015).

### 5.2. Peat formation pattern

The vertical peat growth rates (PGRs) show that growth of the bog has been continuous but at variable rates. For the period prior to 5.5 cal. ka BP, the PGR ( $0.9 \text{ mm yr}^{-1}$ ) was very stable, increasing gradually between 5.5 and 3 cal. ka BP and then slightly up to  $1.0 \text{ mm yr}^{-1}$ . The PGR then increased rapidly between 3 cal. ka BP and 1.5 cal. ka BP, reaching  $1.2 \text{ mm yr}^{-1}$  and remaining stable at this level until 600 cal. yr BP. Later, the PGR increased sharply, to  $1.6 \text{ mm yr}^{-1}$ . The data verify that the temporal resolution of the CVM ( $11 \text{ yr cm}^{-1}$ ) core is the highest of the Iberian peatlands with available information (Pontevedra-Pombal et al., 2017). The growth

rate is similar to those reported for peatlands such as the Walton Moss raised bog in England (Hughes et al., 2000), Langlands Moss in Scotland (Langdon and Barber, 2005) and Store Mosse in Sweden (Malmer and Wallén, 2004). These peatlands have been key to developing the palaeoenvironmental models of northern Europe, and the essential methodologies for environmental reconstruction (Svensson, 1988; Barber et al., 1998; Langdon and Barber, 2005). The models of climate fluctuations of the last 10,000 years, obtained from their study, could not so far be contrasted in similar archives of the southernmost latitudes.

The mean growth rate of the Iberian peatlands (Pontevedra-Pombal, 2002; Pontevedra-Pombal et al., 2017) is  $25\text{--}32 \text{ yr cm}^{-1}$  ( $0.41\text{--}0.31 \text{ mm yr}^{-1}$ ), with the highest mean values in the raised bogs ( $21 \text{ yr cm}^{-1}$ ;  $0.47 \text{ mm yr}^{-1}$ ). The mean vertical growth rate of the CVM bog throughout the Holocene is  $0.91 \text{ mm yr}^{-1}$  ( $11 \text{ yr cm}^{-1}$ ), which is much higher than the mean value for all Iberian peatlands and most other peatlands studied throughout the world and only comparable to the rates established for northern European ones (Aaby, 1986; Silvola, 1986; Ovenden, 1990; Botch et al., 1995).

### 5.3. Climate control in carbon accumulation

The mean Holocene LORCA value for NW Iberian peatlands, including fens and bogs, is  $37.5 \pm 14.6 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Pontevedra-Pombal et al., 2006), higher than the global value proposed for peatlands ( $20 \text{ g C m}^{-2} \text{ yr}^{-1}$ ; Armentano and Menges, 1986) or for the northern peatlands in the northern hemisphere ( $23 \text{ g C m}^{-2} \text{ yr}^{-1}$ ; Loisel et al., 2014) and is slightly lower than the rates calculated for British peatlands ( $40\text{--}70 \text{ g C m}^{-2} \text{ yr}^{-1}$ ; Immirzi et al., 1992).

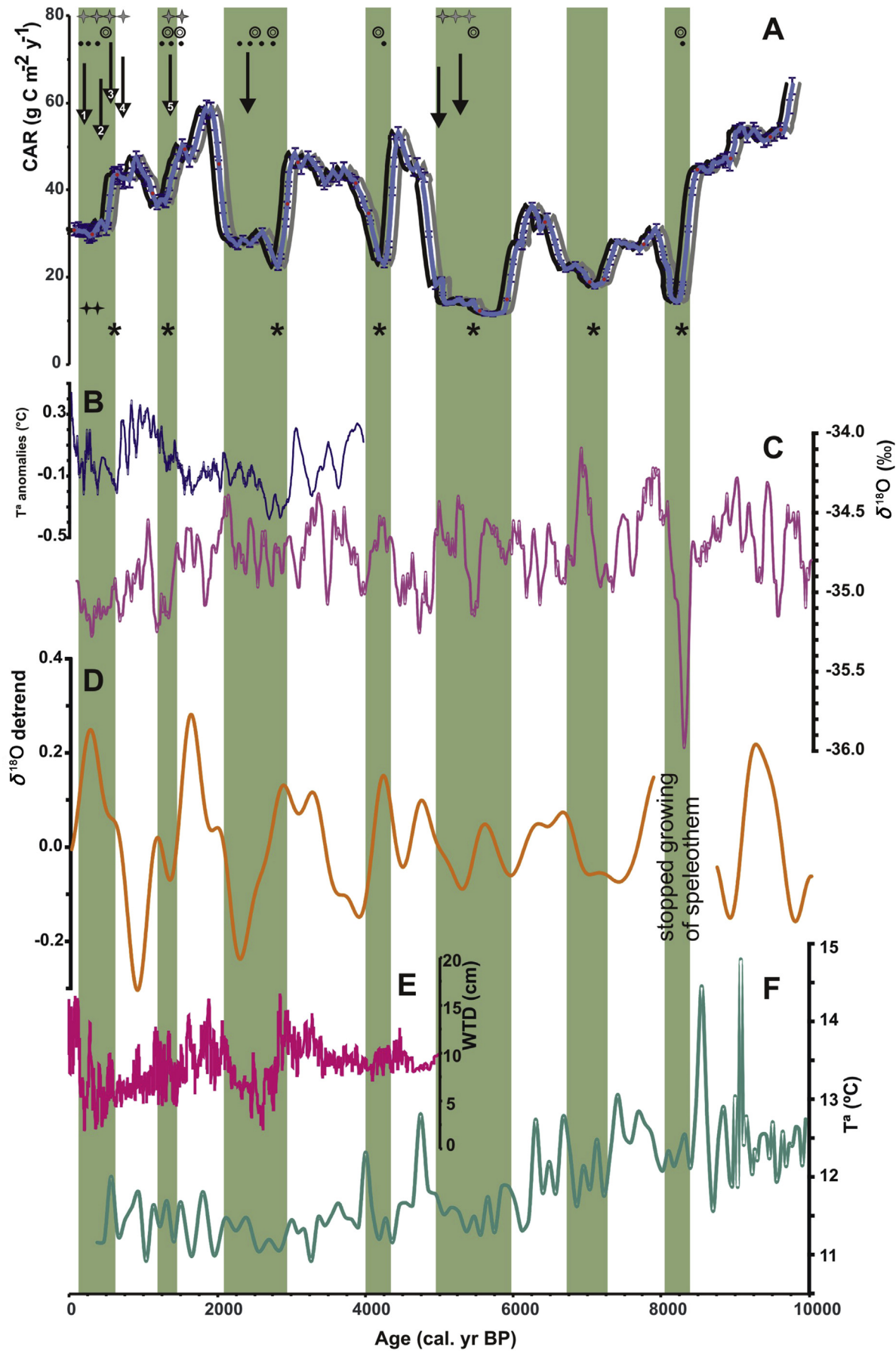
Calculation of carbon accumulation rates in Iberian peatlands, distinguishing between fens and bogs, revealed higher mean values ( $39.8 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) for bogs than for fens ( $29.3 \text{ g C m}^{-2} \text{ yr}^{-1}$ ), as previously reported for peatlands in Finland, Estonia and the USA by Korhola (1995). The mean rates in Iberian bogs are higher than those established for Scottish and Danish ombrotrophic peatlands (Mauquoy et al., 2002) and northern Scandinavian bogs ( $20\text{--}30 \text{ g C m}^{-2} \text{ yr}^{-1}$ ; Tolonen, 1979) but similar to those calculated for Siberian ( $20\text{--}40 \text{ g C m}^{-2} \text{ yr}^{-1}$ ; Botch and Masing, 1983) and Finnish peatlands ( $13\text{--}41 \text{ g C m}^{-2} \text{ yr}^{-1}$ ; Tolonen et al., 1992).

The C accumulation rates are much higher in the CVM raised bog (CAR:  $35.3 \pm 12 \text{ g C m}^{-2} \text{ yr}^{-1}$ ; LORCA:  $59.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) than in the other Iberian peatlands and are amongst the highest rates determined for any peatlands in the northern hemisphere (Gorham, 1991; Vitt et al., 2000; Gorham et al., 2003; Hargreaves et al., 2003; Belyea and Malmer, 2004; Turunen et al., 2004; Yu, 2006; Roulet et al., 2007; Loisel et al., 2014), although comparison of the LORCA values in different types of peatlands and thicknesses must be considered carefully (Lindsay, 2010).

The CAR values calculated for the CVM raised bog along the Holocene describe a variable evolutionary pattern (Fig. 7). The variations are associated with allogenic and autogenic factors (Aaby and Tauber, 1974; Svensson, 1988; Laiho, 2006) that affect, in a cascade reaction, the behaviour of the water level, microbial activity and organic matter evolution. This process is closely linked to climatic oscillations and increasingly to anthropogenic effects, at both local and global scales. In response to this coupling, the dynamics of carbon accumulation in peatlands vary in relation to their type, location and local characteristics (Sakovets and Germanova, 1992; Minkkinen et al., 2002; Moore et al., 2002).

One of the phases of highest C accumulation ( $65 \text{ g C m}^{-2} \text{ yr}^{-1}$ ), relative to the mean accumulation ( $35.3 \pm 12 \text{ g C m}^{-2} \text{ yr}^{-1}$ ), occurred at the start of the peat formation in the CVM record (Fig. 7), coinciding with the climate warming at the beginning of





the Holocene. The accumulation continued, although at a slower rate ( $47 \text{ g C m}^{-2} \text{ yr}^{-1}$ ), until ca. 8 cal. ka BP.

The warm and humid conditions of this period, result of insolation forcing and consequent ice-sheet retreat, have been described on a global (Roberts et al., 2004) and regional scale (Allen et al., 1996; Morellón et al., 2009). These climatic conditions are conducive to an increase in the rates of carbon accumulation.

At local and regional levels, increased accumulation of soil organic matter, increased plant cover, formation of A horizons and - at the optimal Hypsithermal stage (increase from 2 to 3 °C and greater humidity) - brownification, podzolization and formation of ferro-humic crusts in the soils occurred 9–8 cal. ka BP (Martínez-Cortizas et al., 2007). A phase of genesis and expansion of fens and bogs in the NW Iberian Peninsula (Pontevedra-Pombal et al., 2006) and of raised bogs in Ireland and England (Hughes and Barber, 2004) was recorded at approximately the same time as a predominance of biotic and geochemical markers of increased hydrologic levels in mountain (Moreno et al., 2011) and coastal lakes (Costas et al., 2009) in the northern Iberian Peninsula. It has been suggested that the most intense genesis of peatlands in the northern hemisphere occurred within this time frame (Ruppel et al., 2013).

Within this trend of general expansion, Charman et al. (2015) detected a partial decline in the development of northern peatlands. This blockage in the expansion of northern Europe's peatlands is detected in CVM bog as an intense and sharp drop in carbon accumulation. This crisis coincided with an abrupt global climate change event, characterized by extreme cold and variable humidity, which lasted between 600 and 400 years and centred between 8.2 and 8.1 cal. ka BP (Alley et al., 1997; Barber et al., 1999; Alley and Ágústssdóttir, 2005; Thomas et al., 2007). This type of strong climate pulsation has been linked to variations in solar activity (Magny, 2004) or more likely as a response to intense changes in the strength of the Northern Atlantic thermohaline circulation (Head et al., 2006). For the aforementioned period, this has been related to the last great input of freshwater in the North Atlantic derived from thawing of the Laurentide layer and drainage of the large associated lakes (Clark et al., 2001).

The conditions and duration of the 8.2 ka event appear to indicate an intense geographic modulation (Rohling and Palike, 2005). The impact of this climatic event has been widely recorded in northern latitudes between 55° and 61° (Seppä et al., 2007), but scarcely recorded at mid latitudes, for which Magny et al. (2003) proposed the existence of humid conditions, possibly favouring peat accumulation.

Although the climate reconstructions for the Iberian Peninsula indicate that this event is absent from most stratigraphic sequences due to lack of temporal resolution (Muñoz-Sobrino et al., 2005; Cacho et al., 2010; Ortiz et al., 2010), it has been usually related to arid conditions (López-Saéz et al., 2008; Martínez-Cortizas et al., 2009; Morellón et al., 2009; Ortiz et al., 2010; Moreno et al., 2011; Aranbarri et al., 2014). The cold and arid conditions are unfavourable to the evolution of the peat and, consequently, to the accumulation of carbon-rich organic fractions.

At CVM a dramatic reduction in the C accumulation rate was recorded during the 8.2 ka event (Fig. 7), with a CAR of  $19 \text{ g C m}^{-2} \text{ yr}^{-1}$  between 8.3 and 8 cal. ka BP. This CAR supposes a reduction of 70% to 40% of the preceding rates for the period 10–8.3 cal. ka BP.

At the end of this cold event, a phase of intense variability in the carbon accumulation is observed, with two periods of increase in the CAR between 8.0 and 7.3 cal. ka BP, and 6.5 and 6 cal. ka BP respectively. These periods are interspersed with a significant drop in the CAR between 7.2 and 6.8 cal. ka BP. The reconstruction of the sea surface temperature (SST) from marine sediments in the southeast sector of the Bay of Biscay (Mary et al., 2017) and from the inner shelf of the Tagus River Estuary in the Portuguese Margin (Rodrigues et al., 2009), identify a cold anomaly centered on 7 cal. ka BP, which have been associated with periods of strong negative North Atlantic Oscillation (NAO).

In the following millennium, 6.0 to 4.9 cal. ka BP, the carbon accumulation rate was the lowest ( $13 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) recorded during the Holocene (Fig. 7).

This relapse of carbon accumulation in CVM coincides with a phase of global climate detriment known as Neoglaciation (Magny et al., 2006), characterized by a period of gradual global cooling accompanied by drier conditions that occurred ca. 5.5 cal. yr BP and that marked the climate evolution in the next 1000–1500 years.

In this period, several grand minima of solar activity (Usoskin et al., 2007), indicators of abrupt climates crises of global scale (Steinilber et al., 2012) and a glacial advance of supra-regional scale (Wanner et al., 2008) has been identified.

In synchrony with Neoglaciation, the climate reconstructions from the NW Iberian Peninsula indicate a decrease in temperature of 1–2 °C from the Hypsithermal phase until 4.7 cal. ka BP (Martínez-Cortizas et al., 1999), when humidity was also minimal. This event has also been recorded in other Iberian peatlands (Ortiz et al., 2010) and northern peatlands in Europe and North America (Loisel et al., 2014).

A phase of notable recovery in C accumulation rates occurred 5–3 cal. ka BP, reaching a maximum of  $54 \text{ g C m}^{-2} \text{ yr}^{-1}$ . Climate recovery during this period, reaching optimal values ca. 4.4 cal. ka BP and, although colder and drier pulses occurred (Martínez-Cortizas et al., 1999; Fábregas et al., 2003). This climatic improvement has been detected in Iberian and northern European palaeoenvironmental records (Magny, 2004; Ortiz et al., 2010; Moreno et al., 2011; Ruppel et al., 2013), as well as in marine sediments on the Atlantic coast of Galicia (Bernárdez et al., 2008). However, during this period of climate recovery, the CAR in the CVM core dropped strongly below  $22 \text{ g C m}^{-2} \text{ yr}^{-1}$  in an interval centred around 4.2 cal. ka BP. The abrupt '4.2 cal. ka BP' climate change was recorded on a global scale (Bond et al., 2001) as an extremely cold event with latitudinal contrasts in moisture characteristics (Roland et al., 2014). Knowledge of the impact of this event in the northern European and Iberian peatlands is still incomplete (Roland et al., 2014; Lillios et al., 2016) although it has been detected from SST data in sediments of the Iberian littoral (Rodrigues et al., 2009; Mary et al., 2017).

**Figure 7.** (A) Carbon accumulation rates (CAR) in Chao de Veiga Mol bog at the last ten millennia (excluding the acrotelm). From chronological model: blue line, most probably age; grey and black lines minimum and maximum age intervals respectively; red dots indicate the position of the  $^{14}\text{C}$  dates; blue vertical bars show the uncertainty of the calculated CAR. Green areas indicate relapses of C accumulation coinciding with climatic cooling phases. The arrows mark grand minima of solar activity (from Usoskin et al., 2007): 1–Dalton, 2–Maunder, 3–Spörer, 4–Wolf, 5–Oort; the empty circles with double line mark global indicators of abrupt climates changes (from Ljungqvist, 2010; Wanner et al., 2011, 2014; Steinilber et al., 2012); the full circles mark regional indicators of abrupt climates changes (from Desprat et al., 2003; Swindles et al., 2007; Bernárdez et al., 2008; Moreno et al., 2011); the gray stars indicate supraregional neoglaciation glacier advances (from Wanner et al., 2008); the black stars indicate local glacier advances (from González-Trueba et al., 2008; Serrano et al., 2013); the asterisks mark cold anomalies of the surface sea temperature in marine sediments of Iberian littoral (from Rodrigues et al., 2009; Mary et al., 2017). (B) Anomalies of land surface temperature in Northern Iberia during middle Holocene (Martín-Chivelet et al., 2011; ENCI, 2018). (C) Holocene evolution of isotopic oxygen fractionation in the Greenland GISP2 core (Stuiver et al., 1997; ENCI, 2018). (D) Speleothem  $\delta^{18}\text{O}$  records from a cave on the Atlantic coastline of northern Iberia (Smith et al., 2016; ENCI, 2018). (E) Variation of the water table in Ireland's peatlands from the Middle Holocene (Swindles et al., 2013; ENCI, 2018). (F) Temperature fluctuation in the northeast Atlantic during the Holocene (Sundqvist et al., 2014; ENCI, 2018).

The rate of C accumulation again fell well below the mean CAR value during 3–2 cal. ka BP (Fig. 7). The decrease in the accumulation rates detected 3000 years ago appears to be widely distributed, being identified in most of northern peatlands in the northern hemisphere (Loisel et al., 2014). It is a very cold event that has been identified in the pollen records and marine sediments of the northwest of the Iberian Peninsula (Desprat et al., 2003; Rodrigues et al., 2009; Mary et al., 2017). This thermal relapse coincides with the identification of a grand minima of solar activity (Usoskin et al., 2007). In this period, the minimum CAR in CVM occurred around 2.8 cal. ka BP. This signal coincides with an abrupt climate change to colder conditions that lasted approximately 100 years and that has been detected in European peatlands in northern to temperate zones (Yu, 2006; Chambers and Daniell, 2010).

The period of fastest C accumulation ( $58 \text{ g C m}^{-2} \text{ yr}^{-1}$ ), except for the beginning of the bog formation, occurred 2–1.5 cal. ka BP. This could be related to a marked wet and warm event also recorded in other ombrotrophic peatlands close to the CVM (Martínez-Cortizas et al., 1999; López-Días et al., 2010; Ortiz et al., 2010; Castro et al., 2015), but also on a global scale throughout the entire supra-tropical sector of the northern hemisphere (Ljungqvist, 2010). This event corresponds to the well-known Roman Warm Period. The increase in C accumulation rates towards the start of the last millennium matched with that observed in rain-fed peatlands in the British Isles and central Europe (Mauquoy et al., 2002).

The next significant drop in carbon accumulation in CVM was identified between 1.4 and 1.2 cal. ka BP. This decrease in the CAR coincides with a period of cold and arid conditions known as Dark Ages or Migration Period Cooling (500–1000 cal. AD; Lamb, 1985). This abrupt climate change has been isolated from multiple records of the Northern hemisphere (Ljungqvist, 2010), however its detection in the Iberian Peninsula is scarce, and essentially in marine sediments (Desprat et al., 2003; Bernárdez et al., 2008; Mary et al., 2017).

The increase of the CAR in CVM bog showed a dry and warm phase between 1.2 and 0.75 cal. ka BP, coinciding with the Medieval Climate Anomaly of the northern hemisphere (Bond et al., 2001; Ljungqvist, 2010; Wanner et al., 2014). This event episode has also been recorded on a local (Martínez-Cortizas et al., 1999; López-Sáez et al., 2014; Castro et al., 2015) and regional (Desprat et al., 2003; Rodrigues et al., 2009; Moreno et al., 2011) scale. These climatic conditions are probably associated with a combination of high solar and low volcanic activity and a positive NAO phase (Sánchez-López et al., 2016).

A new decrease in C accumulation rates was detected in the CVM for the period between ca. 650 and 250 cal. yr BP (Fig. 7). This period corresponds globally to the climatic event known as the Little Ice Age (ca. 675–100 cal. yr BP; Mann et al., 1999), although in our case the C accumulation rates were only established for the catotelm—the output from the LIA was not analysed and a multiproxy estimation approach would be required. This cooling period coincides with a high volcanic activity and the development of four remarkable Grand Solar Minima (Wolf, Spörer, Maunder and Dalton Minima).

During this period, the information recorded at regional scale indicates extremely cold conditions, especially anomalous in summer, and an increase in construction of snow wells (Fernández-Cortizo, 1996), and wet and climatic conditions were recorded throughout the entire Iberian Peninsula (Sánchez-López et al., 2016). In peatlands close to the study area, molecular (López-Días et al., 2010) and geochemical (Martínez-Cortizas et al., 1999) markers identify a cold phase with oscillations in moisture and temperature. This climate phase also caused an acute decrease in C accumulation in raised bogs in Sweden (Malmer and Wallén, 2004),

Denmark and England (Mauquoy et al., 2002) and in the northern European peatlands in general (Charman et al., 2013).

## 6. Conclusions

The evolutionary model for the Chao de Veiga Mol raised bog identifies this peatland as a high resolution palaeoenvironmental archive for the entire Holocene, with high growth rates (mean PGR  $11 \text{ yr cm}^{-1}$ ) that at least duplicate those in previously studied Iberian peatlands and that are higher than those reported for peatlands in the northern hemisphere.

The dynamics of temporal and biogeochemical development potentially enable more precise analysis of the effects of different global Holocene climatic events that are not well known in southern Europe, especially in relation to regional and local modulation.

The data indicate that, in contrast to what was previously assumed for temperate peatlands, the rate of carbon accumulation in the CVM raised bog is higher than the mean value for peatlands in the northern hemisphere, probably as a result of the increase in recalcitrant C-rich compounds, which are generally resistant to the effects of climate warming.

The pattern of carbon accumulation rates during the Holocene in Chao de Veiga Mol raised bog showed synchronous variations with all the main climatic events described in the northern hemisphere and strongly coinciding with the models established for the northernmost latitudes: (1) climate recovery, peatland formation and/or increase in carbon accumulation in the periods of ca. 10–8.2, 8–7.3, 6.5–6, 5–3, 2–1.5 and 1.2–0.75 cal. ka BP; (2) reduction in carbon accumulation in the periods of ca. 8.25–8.1, 7.2–6.8, 6–4.9, 4.3–4.1, 3–2.1, 1.4–1.2 and 0.65–0.25 cal. ka BP; (3) records of the impact of abrupt climate changes around ca. 8.2 ka, 7.0 ka, neoglaciation, 4.2 ka, 2.8 ka, Dark Ages and LIA; (4) record of the beginning of the first effects of the LIA in the NW of Iberian Peninsula at the mid-14th.

The high potential of this mire as a record of the Holocene environmental evolution will allow improved the detail on the intensity, duration and extension of the different episodes of abrupt climate change in the Iberian Peninsula, through multiproxy analysis, both geochemical (isotopes, organic compounds, trace elements) as biotic (pollen, diatoms, testate amoebae, macrofossils).

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